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14. ABSTRACT

We have developed first principles methods for the design of structural materials based on the concept of "objective structures". This concept embraces many of the structures such as nanotubes and buckyballs, as well as emerging nanosheets, nanosprings, nanorings, nanoribbons, nanocapsules and nanorods that comprise the main structures of nanotechnology. We have discovered new methods to directly compute the elastic behavior and strength of these structures, with our main applications to carbon nanotubes (of various chirality) and to graphene sheets. The main instabilities under bending and torsion have been elucidated and quantified, including the effects of twist and bending on band gap. A surprising failure behavior of carbon nanotubes in tension was discovered involving premature failure at intermediate strain rates. Finally, a proposal for the design of new testing machines for fluids at high rates of strain was given, in which the macroscopic fluid behavior can be directly related to an atomistic simulation. This simulation encompasses extreme effects such as chemical reaction and dissociation.

15. SUBJECT TERMS
Nanotechnology, multiscale methods, first-principles methods, structural materials, carbon nanotubes, graphene sheets

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MULTISCALE METHODS FOR THE DESIGN OF STRUCTURAL MATERIALS FROM FIRST PRINCIPLES

Systematic search for new nanostructures with
unprecedented mechanical properties

Final report for **AFOSR-FA9550-09-0339** and for **Multiscale Methods For The Systematic Analysis And Design Of Nanostructures And Nanostructured Materials FA9550-09-1-0393** submitted to Dr. Fariba Fahroo of the Air Force Office of Scientific Research
March 15, 2012

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1 Introduction

This is a report of progress on the project AFOSR-FA9550-09-0339, **Multiscale methods for the design of structural materials from first principles**.

There is a remarkable qualitative similarity of the main structures of nanotechnology. This is true of the structures – carbon nanotubes and buckyballs – that originally defined the field. But, during the period of this project, as more complex nanosheets, nanosprings, nanorings, nanoribbons, nanocapsules, and nanorods have emerged, it has become increasingly clear that both their existence and their remarkable properties are a direct result of the defining property of objective structures: that corresponding atoms in each molecule see precisely the same environment up to translation and rotation. Thus we are increasingly convinced that the mathematical theory of objective structures comprises *the quantitative, predictive* approach to nanotechnology.

Through the results of this project, it is also become increasingly clear to us that the essential aspect of Objective Structures is not the "structure" itself. Rather it is about the "invariance" – the fundamental invariance of physical theories. This is the origin of the reason that objective structures form in the first place, often by the process of self-assembly, and also the reason for their remarkable properties. Using this invariance we have been able to describe quantitatively the main instabilities of carbon nanotubes in bending and torsion, we have been able to predict and understand how deformation can have a strong effect on bandgap. We found that torsion is particularly effective.

We have also discovered a fundamental invariant manifold in the equations of molecular dynamics. This manifold can be written down explicitly and is independent of the atomic forces. If one chooses initial conditions for the equations of molecular dynamics on this manifold, then the corresponding solution rigorously stays on this manifold. The manifold has the same form for a

very simple model of atomic forces like pair-potentials as it does for atomic forces coming from the Hellmann-Feynman theorem based on full Born-Oppenheimer quantum mechanics. The manifold also depends on time in an explicit way. The effect of this is that there are certain overall atomic motions that arise from solutions on this manifold. A major thrust of our work is understanding and exploiting this manifold.

While our project has focused on the development of powerful new computational methods that can apply broadly to problems in nanotechnology, we have tested these methods on problems of significant practical interest. Thus, we have achieved a comprehensive understanding of the mechanical behavior and instabilities in carbon nanotubes, under tension, torsion and bending. Some of our predictions in this area have motivated, and have been confirmed by, subsequent experiments. Further experiments are planned, especially in the dynamic regime. We have found an unexpected link to experimental fluid mechanics, and we believe that our predicted flows will have a paradigm changing effect on the measurement of fluid properties.

1.1 Summary of goals of the project

1. Systematic search for new nanostructures based on objective density functional theory.

2. Dynamic properties and failure modes of nanostructures based on objective molecular dynamics.

3. Exploratory research on the relation of full quantum mechanics to density functional theory.

We have made progress on all three areas. Items 1 and 2 has been especially fertile. Unexpected discoveries were made on the electronic and thermoelastic properties of carbon nanotubes, and on applications of our methods to experimental fluid mechanics. This report is a brief summary of the highlights of our research. More details and further developments can be found in the original papers.

2 Progress

2.1 Objective tight binding and density functional theory

This task concerns the development of a first principles approach to the calculation of the structure and energy of objective structures. Overall, this has the significant advantage over semi-empirical description of atomic forces (like the Tersoff-Brenner potential for carbon) that the answers are expected to have a reasonably high degree of quantitative reliability.

Early in the project we divided the task of writing a objective first principles method into two steps: first, an objective tight binding (OTB) method and, second, a full objective density functional theory (ODFT) method. The development of an OTB method allowed us to confront several issues common to OTB and ODFT, such as the formulation of a Bloch theorem appropriate to objective structures. In addition, OTB is a substantial simplification of ODFT, allowing for detailed study of its predictions for the instabilities of carbon nanotubes [15, 16, 19, 20]. A typical result is shown in Figure 1. These results improve our earlier results [9] on instabilities in torsion using Tersoff potentials. One immediate observation from Figure 1 is that the lowest energy bifurcation from

the cylindrical nanotube yields a highly flattened shape – almost like two ribbons back-to-back – that is observed to be the typical shape of a severely twisted/collapsed carbon nanotube [8]. More importantly, using the OTB method we are able to predict bandgap changes that would not be accessible to empirical atomic forces. This bandgap directly affects the axial electrical conductivity of the nanotube. Our results in Figure 1 correlate well with the measured electrical conductivity of the nanotubes.

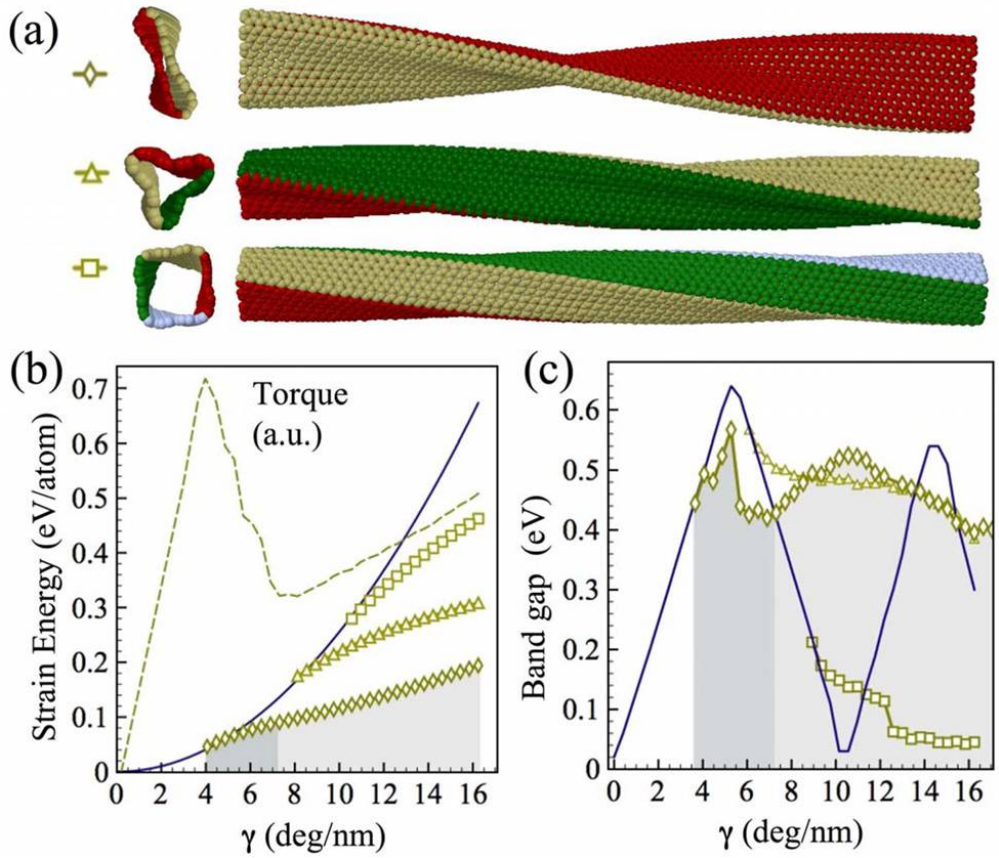


Figure 1: Objective tight binding study of instabilities in torsion of a carbon nanotube. (a) Computed shapes, (b) bifurcation diagram presented as strain energy vs. twist per unit length γ, and (c) bandgap vs. γ.

By carefully studying this response we have realized that the bandgaps of deformed structures, like twisted and bent nanotubes, are essentially determined by a particular scalar effective strain. This correlation is even maintained beyond the rippling instability. This is most clearly illustrated in our study of the twisting of graphene nanoribbons, which avoid the edge effects (where the red and tan regions meet in Figure 1) of nanotubes. Interestingly, when plotted against the effective strain, the bandgap variation of the ribbon is equivalent to that of a seamless carbon nanotube in tension, Figure 2. Thus, our findings [17, 18, 19, 20] establish links between the electronic properties of these three important nanostructures: twisted/collapsed tube, twisted ribbon and ribbon in tension. These results have important implications for the projected uses of nanoribbons as sensors.

We have also used OTB to study the propagation of dislocations in carbon nanotubes [15]. These

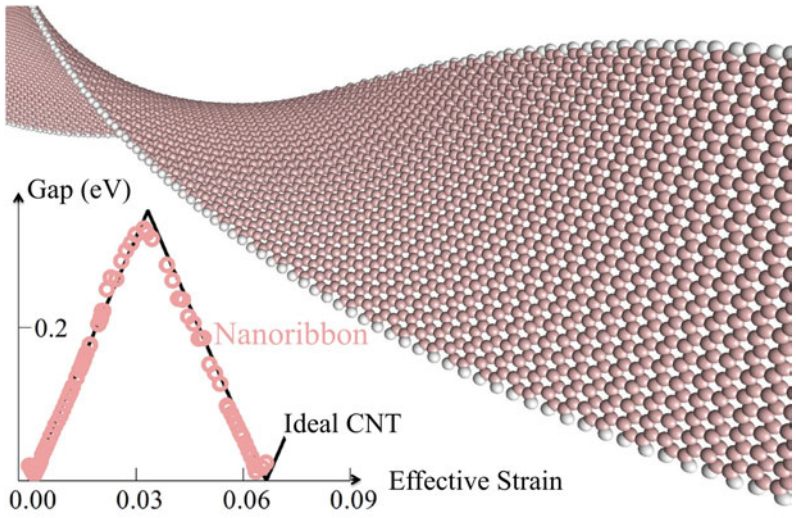


Figure 2: Objective tight binding study of bandgap vs. our effective strain parameter in graphene nanoribbons. The solid curve in the inset corresponds to bandgaps calculated from infinite graphene sheets in uniaxial tension, plotted vs. effective strain.

results, together with a version of transition state theory, give predictions on the failure of carbon nanotubes at very low strain rates that are currently inaccessible to our direct dynamic methods.

We have formulated numerical schemes based on the spectral discretization of Kohn-Sham density functional theory using basis sets adapted to the symmetry of objective structures. A key development in this area has been the implementation of a generalized Fourier transform over the symmetry group of the objective structure and the study of how this transform simplifies the electronic structure computational problem. We have successfully developed a robust spectral code based on these ideas.

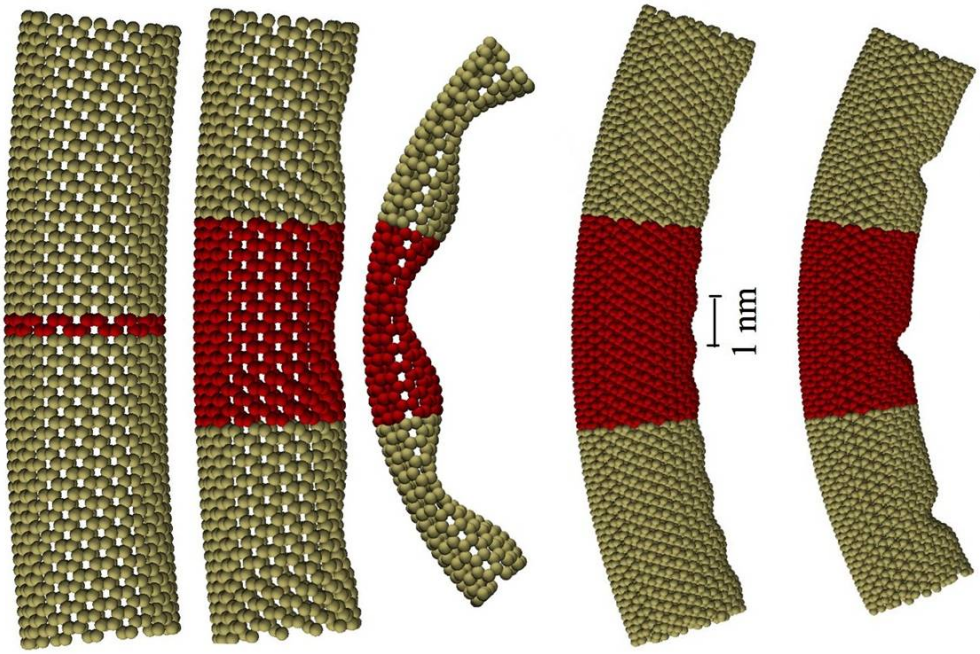
2.2 Studies of the effect of the choice of the fundamental domain

In all of the studies described above we actually only simulate a very small set of atoms, typically, in the examples shown above, a single transverse line or a one-atom-wide ring of 10-20 atoms. The other infinite number of atoms in the figures exactly satisfy the equations of molecular dynamics, according to the basic theorem of OMD. (In the static case the conclusion is that all atoms are in equilibrium.) Can we understand the minimum number of simulated atoms we actually need to express the first bifurcation? In atomic scale problems the wavelengths of the finest scale instabilities are expected to be determined by atomistic length scales. Can we predict those length scales?

As a typical scenario, according to the continuum theory of nonlinear elasticity, we expect under pure bending to see a rippling of the inside of a tube or cylinder under bending [7]. But the wavelength, at least in some cases, is predicted by nonlinear elasticity to be infinitesimal. (This phenomenon is related to the failure of the so-called *complementing condition* [14] of partial differential equations, based on the linearized moduli.) At atomic level we might also expect to see this kind of rippling but with a wavelength now determined by atomic scale.

We are approaching these issues in general from the point of view of bifurcation theory [3, 12]. The computational results illustrate the typical behavior consistent with this theory. Figure 3(a)

shows two fundamental domains (FD) and corresponding simulated atoms (in red) in a single-walled nanotube. Our studies summarized by Figure 3(a) show that the first bifurcation is nicely captured by the larger FD, but not the smaller one. (This smaller FD gives exact solutions but misses the bifurcations to lower energy states.) In multi-walled nanotubes Figure 3(b) a short wavelength rippled mode is seen first, then a widely spaced kink mode, both nicely captured by the larger FD. A change of slope occurs on the graph of moment vs. curvature at the point where rippling occurs [12].



(a) Single walled (15,15) nanotube: two FDs and a severely bent nanotube

(b) Multi-walled (5,5)@(10,10)@ (15,15) nanotube: rippling instability (left), and subsequent kink instability (right)

Figure 3: Systematic study of the effect of the fundamental domain on instabilities in bending. See text.

Subsequent to our work, an experimental group (Jackman, Krakhmalev and Svensson [10]) studied the bending stiffness of carbon nanotubes. An issue with all experiments on carbon nanotubes is that samples often contain both mixed chiralities as well as mixed single/multiwalled samples. The data showed a change of slope in the measured force vs. displacement relations, which the authors correlate rippling of the nanotube. Our data shows the best agreement with the data of the available theories.

2.3 A fundamental invariant manifold in the equations of molecular dynamics

A main discovery of this project is an *invariant manifold* of the equations of molecular dynamics [5]. The discovery is far-reaching, because the manifold can be written down explicitly and it applies to all materials, i.e., it is independent of the atomic forces. A few very special cases were known previously – static periodic boundary conditions and Lees-Edwards boundary conditions for plane Couette flow – but the full manifold is far bigger, richer (lots of free parameters can be varied), and more useful.

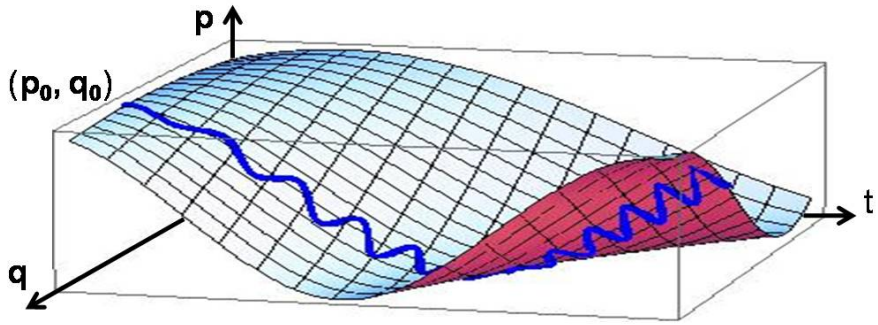


Figure 4: A schematic view of the invariant manifold of Objective Molecular Dynamics.

What is an invariant manifold? This concept from the theory of dynamical systems refers to a generalized surface in phase space (the space of all positions $\mathbf{q} = \mathbf{q}_1, \ldots, \mathbf{q}_N$ and momenta $\mathbf{p} = \mathbf{p}_1, \ldots, \mathbf{p}_N$) such that, if the initial conditions for the equations of molecular dynamics lie on this manifold, the solution stays on this manifold. Our manifold is slightly different in that, in general, it depends on time. However, the time dependence is also completely explicit, and can be written down independently of the atomic forces. A schematic view is shown in Figure 4. All of the motions and static deformations described in this report, nano and macro, lie on this manifold. These are exact solutions. There are no approximations.

What is particularly compelling for multiscale methods is that *most of experimental solid and fluid mechanics*, with one major caveat described below in Section 2.3.3, *lies on this manifold*. It will therefore play a crucial future role for validation of multiscale methods.

The reason classical experimental science evolved in such a way as to lie on this manifold goes to the heart of that subject. The main principle underlying experimental mechanics is to design the testing machine without beforehand knowing the response of the material, and still extract meaningful material properties. This principle is intimately related to the fact that the invariant manifold can be explicitly specified, without beforehand knowing the expressions for the atomic forces.

In this section we describe several examples of studies we have conducted of this manifold in the case the time dependence is nontrivial.

2.3.1 Failure of carbon nanotubes under dynamic loading

An example of the invariant manifold is the use of a helical group with general time dependence. A physical realization of this case is the pulling of a carbon nanotube to failure at constant macroscopic

strain rate. The strain rate can be arbitrarily prescribed. We have noticed [5, 2] quite a few different failure modes.

One main lesson we have learned is about reproducibility. Even restricted to the manifold, there are still infinitely many initial conditions that correspond to a given strain rate and temperature[1]. Generally, we found a lack of reproducibility of, say, strain at failure, by choosing these initial conditions randomly. However, when we ran the dynamical system for a certain period with strain rate equal to zero, until stabilization of the temperature, and then used the stabilized initial conditions (and the measured value of temperature) for subsequent simulations at nonzero strain rate, we obtained remarkable reproducibility. For a given strain rate and temperature determined in this way, the strain at failure varied within $\pm 1/2\%$ of a value, even though this value varied from less than $1/2\%$ to more than 25% with strain rate and initial temperature. Despite the generic complexity of solutions, running the dynamical system for a certain time period seems to have the effect of "preparing" the subsequent initial data, in the spirit of views of O. Penrose [13]. The prepared initial data yields reproducible macroscopic results.

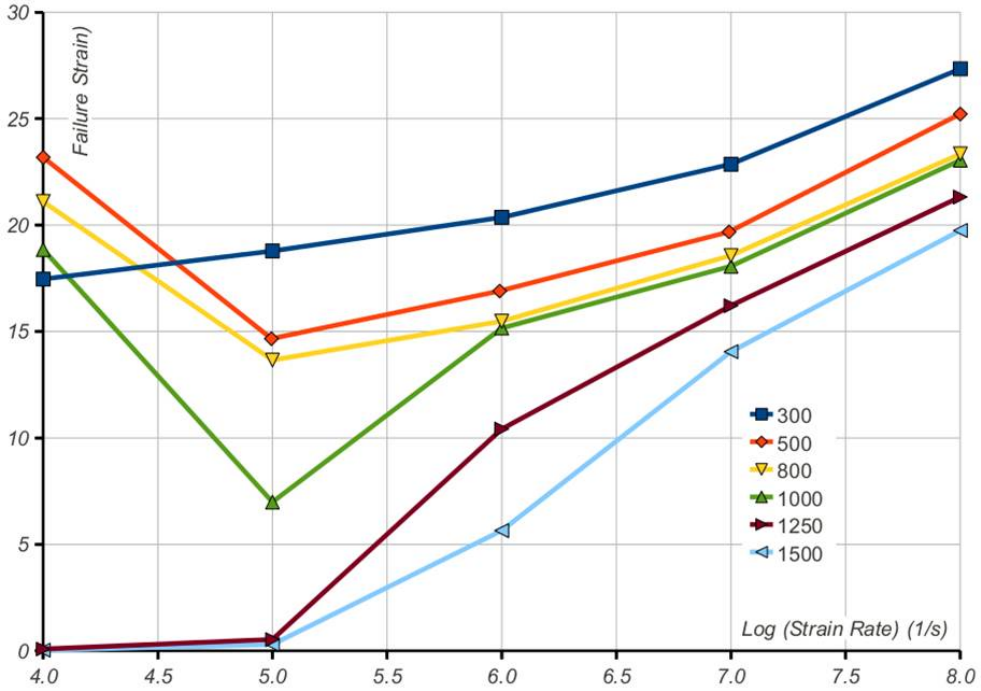


Figure 5: Failure strain as a function of strain rate and temperature measured from simulations.

We saw unexpected failure behavior. Whereas conventional wisdom would say that low strain rates and high temperatures would favor ductility, we found (Figure 5 and [5, 2]) a particular regime of higher temperatures and lower strain rates where the nanotubes experienced a drastic premature failure, at strains of less than a percent! At still lower strain rates, the strain at failure appears to rise again. This highly non thermally activated failure was accompanied by large amplitude oscillations of the cross-section of the nanotube.

[1]calculated as the mean time-averaged kinetic energy of atoms in the FD, after subtracting the mean motion

2.3.2 The entropy of a carbon nanotube

The temperature slightly decreases with time upon first stretching a carbon nanotube at constant strain rate. Thermodynamically, carbon nanotubes behave more like a crystal than a polymer. When we replot temperature, not vs. time, but vs. the current value of strain, as in Figure 6, we see a remarkable collapse of data: the blue and red curves agree over a large region. This is strong indication that, on the indicated domain of temperature and strain, a nonlinear 1D continuum thermoelasticity theory prevails [2]. From this viewpoint these collapsed curves are naturally interpreted as the level curves of entropy density $\eta(\varepsilon, \theta)$ as a function of strain and temperature. This interpretation is also consistent with the the observed evolution of forces.

The conclusion is striking: even though the carbon nanotube is being pulled a very high rates exceeding 10^6/sec, it is behaving, *up to a point*, as a dissipationless thermoelastic material. We have used the data of Figure 6, together with a separate calculation of entropy at $\varepsilon = 0$ to fix the free function of temperature, to fully determine the entropy function of a carbon nanotube.

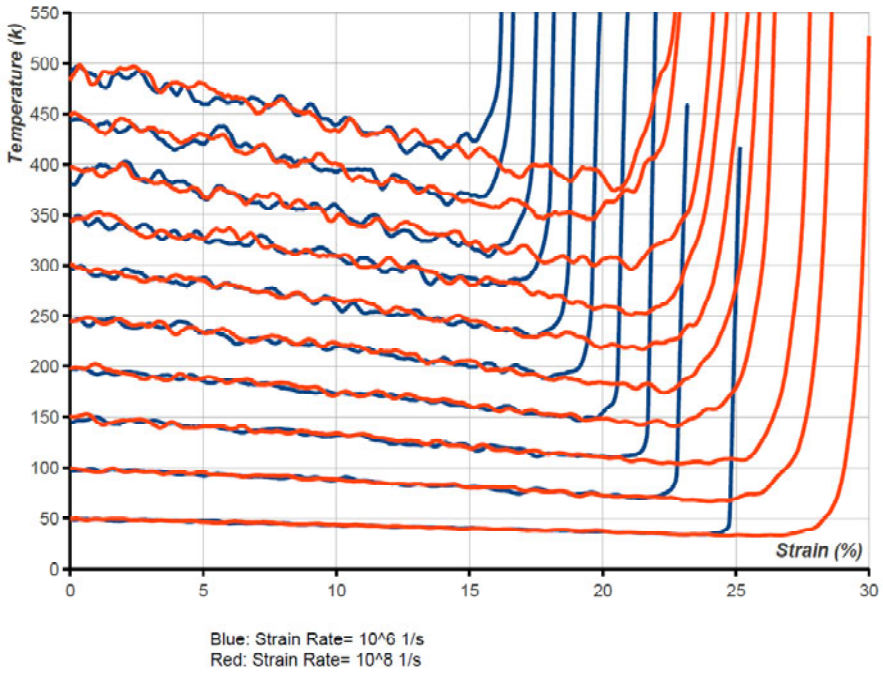


Figure 6: Temperature vs. strain plotted for two different strain rates. Blue: 10^6 per sec. Red: 10^8 per sec. Excellent agreement between these results and 1-D nonlinear thermoelasticity occurs in the domain where the curves overlap: in this region the curves shown are level curves of the entropy function $\eta(\varepsilon, \theta)$.

The red and blue curves of Figure 6 depart from each other somewhat before any obvious sign of failure. We are currently using these curves to understand the key problem of how to model dissipation and failure in carbon nanotubes. Understanding failure initiation, i.e., the point where the red and blue curves of Figure 6 depart from each other, will enable the use of a simple continuum thermoelasticity theory to be used to simulate up to that point, within a multiscale framework.

2.3.3 A new paradigm for experimental fluid mechanics

By the early 1950s it was well appreciated that the Navier-Stokes theory of fluid mechanics did not describe, even qualitatively, many of the features of complex fluids that were playing an increasingly important role in technology, particularly polymer processing. This led to models of "viscoelastic" and other "non-Newtonian" fluids, but also a reassessment of what it means to characterize a complex fluid, beyond its viscosity. On the theoretical side it led to the science of rheology and the theory of viscometry, which in turn led to designs for rheometers and standard procedures for measurement not only of viscosity, but also of normal stress differences.

We have observed that the most basic of these flows, plane Couette flow, lies on our invariant manifold [5, 6]. But we have also seen that other viscometric flows do not. On the other hand we found that there is a large family of flows, those having velocity fields of the form

$$\mathbf{v}(\mathbf{x}, t) = \mathbf{A}(\mathbf{I} + t\mathbf{A})^{-1}\mathbf{x} \tag{1}$$

(for any 3×3 matrix $\mathbf{A}$) that *are* on this manifold. This means we have an efficient molecular level simulation method for these flows. Flows of the form (1) include compressible as well as a 3-parameter family of incompressible flows, with diverse physical phenomena such as unsteady motions, vortices and vortex stretching. Complex phenomena such as combustion and other chemical reactions, breakdown of polymers, dissociation and complex thermodynamics such as occurs in high speed flows are all allowed. These phenomena go far beyond what the state-of-the-art in experimental fluid mechanics is able to characterize.

Unlike viscometric flows, the flows (1) are exact solutions for every accepted continuum model of fluid flow, Newtonian or non-Newtonian. Together with the explicit statistics of the invariant manifold, our invariant manifold gives new solutions of the Boltzmann equation. It is our contention that these flows should be the basis of a new paradigm of experimental fluid mechanics. We have made a first attempt [6] at designing generalized rheometers based on the flows (1).

3 Practical implications of our research for Air Force applications

Our studies of the bandgap of carbon nanotubes vs. bending, twisting and tension provide significant information for the evaluation of carbon nanotubes as sensors. Since it is relatively easy to measure the electrical conductivity of nanotubes, there is the possibility of using nanotubes for accurate measurement of extremely small forces, torques or shear stresses.

The effective scalar strain approach combined with objective MD simulations provides a convenient theoretical platform for understanding the bandgaps in helical nanoribbons. It allows to understand in a unified way the electromechanical response of graphene nanoribbons, fractional carbon nanotubes, and carbon nanotubes. We envision that a Peierls effect we reported can be exploited for switching devices employing narrow nanoribbons with operating points in the vicinity of bandgap closure.

In our dynamic studies of failure at high strain rates we have noticed an unusual regime of premature failure. This has implications for the structural integrity of composites made with carbon nanotubes. This is an active area of research within AFRL, particularly related to the problem of getting the stryength of the composite to benefit from the strength of the nanotube.

Our results have implications for experimental fluid mechanics. We have given a universal method of molecular level simulation that can be used to simulate, with a few atoms, certain large scale flows. This has major potential implications for the Air Force and its contractors. Instead of testing full scale vehicles in elaborate wind tunnel facilities[2] it may be possible to design much simpler, much less expensive, experimental facilities that produce our flows. These can then be used directly to validate an array of computational fluid mechanics and multiscale methods. Of particular interest to the Air Force are flows with chemical reactions (combustion), and high speed flows involving processes like complex thermodynamics, dissociation and excited states.

References including one or more of the authors of this report, with the exception of earlier work [9], were supported by this project.

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